

Thermal Energy Studies. IV. Comparison
of Continuous and Discontinuous Methods
of Measuring Heat Capacities. Heat
Capacities of Some Aliphatic
Bromides

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE
JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY
ROBERT FREEMAN DEESE, JR.
Baltimore, 1929

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ACKNOWLEDGMENT

The author takes pleasure in expressing here his thanks to Dr. Donald H. Andrews for sponsoring this research and his advice given during its progress.



THERMAL ENERGY STUDIES. IV. COMPARISON OF CONTINUOUS AND DISCONTINUOUS METHODS OF MEASURING HEAT CAPACITIES. HEAT CAPACITIES OF SOME ALIPHATIC BROMIDES

One of the major experimental difficulties in the measurement of the heat capacities of organic compounds is the slowness with which thermal equilibrium is established following a change in temperature. Organic compounds in any form are as a rule very poor heat conductors and when occasionally a compound crystallizes in long fine needles or some other state that is hard to pack solidly, it becomes an almost perfect heat insulator. The standard method of heat capacity measurement has always involved bringing the substance to uniform temperature, passing in a known quantity of energy electrically, and waiting for thermal equilibrium to be established at some higher temperature. With a substance of very low heat conductivity this period of waiting frequently becomes so long that heat leaks to the surroundings of the calorimeter practically invalidate the measurement.

To overcome these difficulties a new method based on calibrated heat conduction was developed by Andrews,¹ Haworth² and Smith³ which proved very successful with a number of compounds. This method, however, is a comparative and not an absolute one. It therefore seemed worth while to make a study of an absolute method of heat capacity measurement in which some of these sources of error might be eliminated.

The principle of continuous heating which was used by the authors mentioned above seemed to offer the most favorable possibility of avoiding delays and errors due to poor heat conduction. In the older methods it was generally customary to produce the heat either in a coil wound on the

¹ D. H. Andrews, *J. Am. Chem. Soc.*, **48**, 1287 (1926).

² D. H. Andrews and E. Haworth, *ibid.*, **50**, 2998 (1928).

³ R. H. Smith and D. H. Andrews, *ibid.*, **53**, 3644 (1931).

outside of the calorimeter or in a well inside the calorimeter. Following a suggestion of Dr. George Lynn, formerly of Yale University, it was decided to place the heating unit directly in the material to be studied, using a lattice of platinum wires somewhat similar to the design of Southard and Andrews.⁴

By constructing a calorimeter of this type which could be operated either by continuous or discontinuous heating under identical conditions, it was hoped that light could be thrown on the nature and importance of the errors caused by poor thermal conductivity.

Apparatus

The calorimeter used consisted of a square gold-plated copper can in which the substance to be studied could be placed. This was suspended in a shield which could be brought to any desired temperature and kept constant. This shield was in turn suspended in a vacuum jacket. The shield and vacuum jacket were used in order to obtain the best adiabatic conditions possible. The details of the apparatus, as shown in Fig. 1, and its manipulation will be described below.

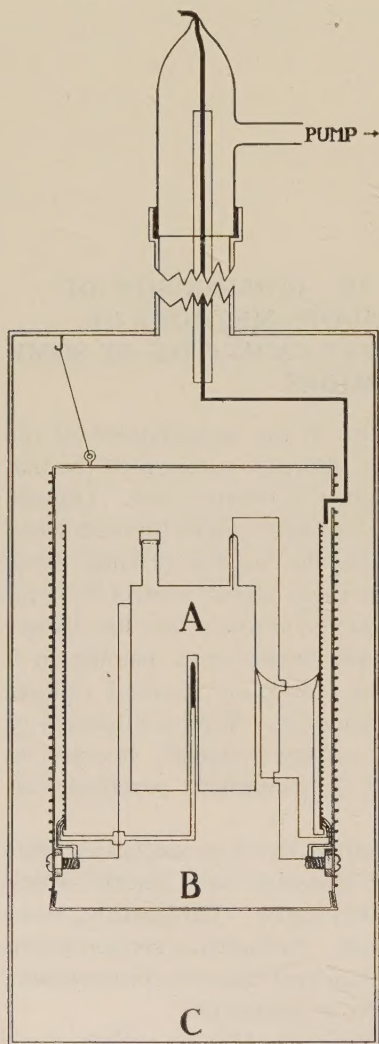


Fig. 1.—The calorimeter.

mercury diffusion pump backed up with a high vacuum oil pump. It was possible to maintain vacuum of approximately 10^{-5} mm. pressure.

The Shield.—The shield (B, Fig. 1) was similar in design to the one constructed by Southard and Andrews⁴ but much larger in dimensions. It was a copper cylinder

⁴ J. C. Southard and D. H. Andrews, *J. Franklin Inst.*, 209, 349 (1930).

11 cm. high, 7 cm. in diameter and 1.5 mm. thick, weighing about 400 g. A heating coil of No. 30 constantan wire (silk insulated), approximately 125 ohms resistance, was wound around this and bakelited on. Some of the wire was wound on the top and the bottom. Near the bottom were placed four small bolts which were electrically insulated from the shield by the use of mica washers and rubber tubing. These were placed there in order that heating leads could be soldered to them, thus eliminating any free joints dangling in the apparatus.

All wires leading to the calorimeter and inside of the shield were wound around a cylindrical sheet of copper three or four times and bakelited to it. This fitted snugly into the shield and was further bakelited to hold it in place. To this inner copper sheet were also bakelited three junctions of a copper-constantan thermel. These were insulated from the copper sheet with silk and wound around it in the same manner as the other wires. To the inner side of the copper sheet, after it had been placed in the shield, was soldered one end of a copper-constantan thermocouple for use as a difference thermocouple, the other end being soldered directly to the calorimeter can. The bottom of the shield fitted tightly and could be removed easily for putting in the calorimeter.

The Calorimeter.—The can itself (A, Fig. 1) was gold-plated copper, $3.2 \times 3.2 \times 5.2$ cm. inside dimensions, with a small tube open to the outside leading about two-thirds of the way up inside for a thermocouple as shown in Fig. 1. It had two openings at diagonal corners. Into one was sealed a piece of No. 20 platinum wire with glass to keep it insulated from the can. The heating unit was placed in the can, one lead being soldered to the can, the other to the platinum wire leading in at the top. The top of the can was then soldered on and the opening for pouring liquids into the can was closed with a small copper cap which was soldered on with low temperature (60°) solder. The thermocouple for measuring the temperature of the calorimeter was wound around a piece of copper wire and soldered to it. This fitted very snugly into the opening at the bottom of the calorimeter can and gave good contact. The other junction of the thermocouple was in an ice-bath on the outside. The calorimeter can was suspended in the shield with heavy thread. Its total weight empty was approximately fifty-three grams.

Heating Unit in Calorimeter Can.—The heating unit was made with the idea of obtaining uniform heating throughout the can. The frame as finally used is shown in Fig. 2 and was made by suspending platinum-iridium wires (0.0025 in. diameter) between two mica plates in spirals. The mica plates were held together by four strips of mica which were so cut at their ends that they would fit into slots in the side of the mica plates and make a frame out of it. The resistance of the wire here amounted to about seventy ohms at room temperature.

The heating leads to the can along with drop across heating coil were connected and soldered at two insulated bolts in the bottom of the shield. Correction was made for drop across the copper wire (No. 29) leads from the can to the bolts.

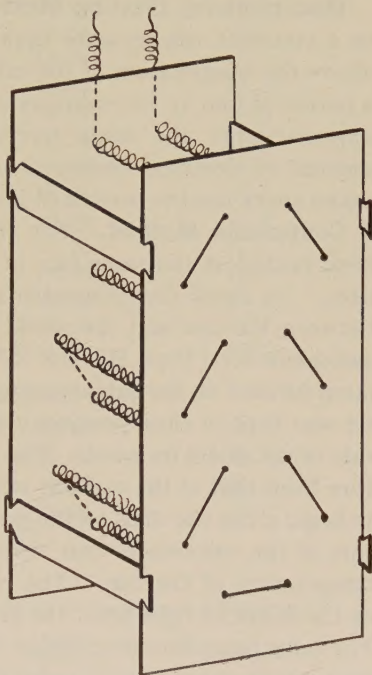


Fig. 2.—The heating unit.

The e. m. f. from the thermocouples was measured with a White potentiometer. The voltage drop across the calibrated resistance coil of manganin wire in series with current gave the amount of current flowing. The voltage drop across the heating unit was measured with a potentiometer hook-up using a Leeds and Northrup recorder to measure the last fifty millivolts.

All thermocouples were made of No. 36 copper and No. 30 constantan wire, both double silk insulated. These were calibrated to conform with the temperature scale of this Laboratory.⁵

Method of Procedure

Discontinuous Heating Method.—This consists in bringing the shield to a constant temperature approximately one to one and a half degrees above the temperature of the calorimeter can. The can is then heated for a period of four to five minutes or the length of time required to carry it to approximately the same temperature above the shield. A measured amount of electrical energy is used. The temperature of the can is then taken every minute here until it comes to equilibrium.

Continuous Method.—For this method the can and the shield were both heated at the same rate of approximately a degree every three minutes. To check the temperature of the shield the difference thermocouple between the can and the shield was connected to a Leeds and Northrup galvanometer (Type HS No. 2285) which had the filament of a tungsten lamp focused on the galvanometer mirror. The beam from the galvanometer was kept in close proximity to the zero point by changing the heating rate of the shield by hand. The maximum deviation of the shield temperature from that of the can was never over two-tenths of a degree. In order to begin a run the dials on the potentiometer corresponding to the temperature of the calorimeter can were set at a few microvolts above the actual temperature of the can. The run was begun by starting the stop watch as the beam of light from the galvanometer mirror passed the zero point. The same procedure was carried out in finishing the run except that another stop watch was started in order to start another run. In this way the heat capacities were measured continuously over the whole range. The runs were usually made over a period of twenty minutes. The average voltage drop across the heating unit in the calorimeter was obtained from the curve plotted by the Leeds and Northrup recorder. The current was determined from the voltage drop across the calibrated resistance coil a number of times during the run and the average value was used in the calculations.

To calculate results the following formula was used

$$\text{Heat capacity (cal./degree)} = (IET/D) \times 0.23912$$

I = current in milliamperes

E = voltage drop across heating unit

⁵ Southard and Andrews, *J. Franklin Inst.*, 207, 323 (1929).

T = time in seconds

D = temperature change (degrees centigrade)

0.23912 = conversion factor joules-calories based on 1 calorie = 4.182 joules

TABLE I
HEAT CAPACITY OF BENZENE

$T, ^\circ\text{K.}$	C_p		
	(a)	(b)	(c)
Continuous Method			
104.21	8.61	12.21	12.5
106.76	8.89	12.76	12.7
115.16	9.34	13.59	13.2
120.60	9.45	13.74	13.6
130.56	9.96	14.59	14.2
135.98	10.17	14.89	14.6
144.15	10.72	15.76	15.2
158.39	11.22	16.13	16.2
159.73	11.55	16.78	16.4
169.95	11.74	16.78	17.2
176.41	12.21	17.55	17.8
184.76	12.63	18.16	18.6
204.09	13.93	20.13	20.5
208.84	14.04	20.46	21.0
227.13	15.48	23.05	23.1
Discontinuous Method			
94.4	9.34	12.415	12.0
164.4	12.55	15.69	16.7
195.76	14.37	19.64	19.7
217.15	15.84	21.94	21.9

TABLE II
HEAT CAPACITY OF CALORIMETER PLUS 52.12 G. OF *n*-BUTYL BROMIDE

Mean temperature, °K.	Cal./degree	Mean temperature	Cal./degree
Discontinuous Heating Method			
179.84	19.51		
186.51	19.51	240.03	19.99
214.03	19.54	247.29	20.28
Continuous Heating Method			
194.51	18.48	228.81	18.83
196.81	18.64	233.74	18.81
203.29	18.48	235.63	18.94
207.89	18.46	240.22	18.86
209.62	18.14	242.36	19.16
214.44	18.43	246.73	19.07
215.98	18.61	248.96	19.17
220.85	18.52	255.45	19.32
222.36	18.52	259.53	19.51

Calibration and Comparison of the Two Methods

In order to obtain the values for the heat capacity of the calorimeter alone it was filled with hydrogen and a number of values were determined by the discontinuous method.

The can was then filled with benzene and specific heat values were determined by both methods. The values given in Table I, column (a), are for the can plus 36.71 g. of benzene. These are shown in Fig. 3, curves 1 (discontinuous method), 2 (continuous method).

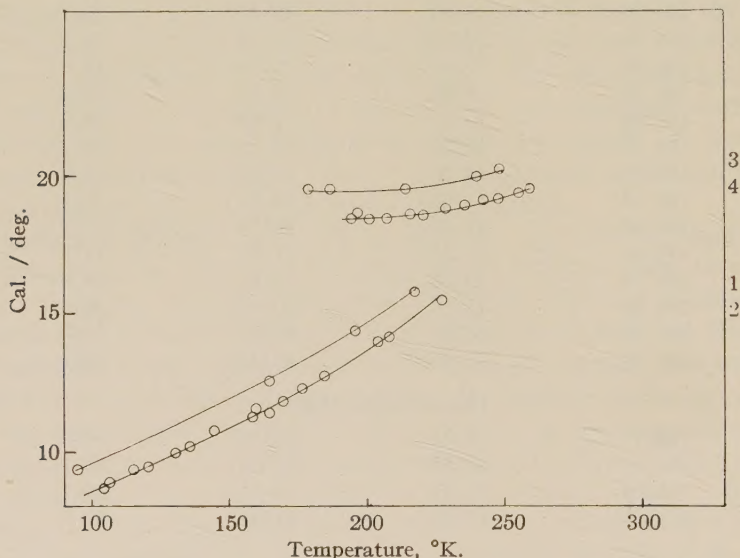


Fig. 3.—Heat capacities of calorimeter plus substance: benzene, (1) discontinuous, (2) continuous method; *n*-butyl bromide, (3) continuous, (4) discontinuous method.

The difference in heat capacity values as determined by the two methods is approximately one calorie throughout the range with benzene. A further comparison of the two methods was made on *n*-butyl bromide between 180 and 250°K. The values obtained are found to be consistent with those for benzene in showing a similar difference in specific heats for the two methods, the difference being approximately one calorie throughout the range. This is shown by curves 3 and 4, Fig. 3. The first (3) gives values obtained by the discontinuous methods. These values are given in Table II.

The difference between the two methods is probably due to a combination of the small errors which are introduced in the method of continuous heating by the constant temperature gradient in the material and by the fact that the average temperature difference between the calorimeter can and its shield is not zero.

It may be seen, however, that by application of a correction factor of one calorie to the calibration, when the continuous method is used, accurate values can be obtained. Table I, column (b), contains the values for the heat capacity of benzene calculated in this manner from the measurements made by the method of continuous heating; values obtained by the method of discontinuous heating are also included. For purposes of comparison values interpolated from the measurements of Huffman, Parks and Daniels⁶ and from Nernst⁷ are also included, column (c). It is clear that there is good agreement between the two sets of observations. We may therefore conclude that the method of continuous heating is dependable and of about the same order of accuracy as the discontinuous method. When one considers the advantage of obtaining measurements over the whole temperature range without leaving any gaps and with less time and labor as compared with the discontinuous method, it may be concluded that this method should prove valuable in a number of cases. As compared with the method of calibrated heat conduction, this method has the advantage of making possible the measurement of the heat of fusion directly in the apparatus. With compounds for which abnormal thermal effects occur, it permits a study of the phenomenon in a number of different ways under carefully controlled conditions.

Heat Capacities of Normal Butyl, Normal Amyl and Normal Hexyl Bromides

Preparation of Compounds.—Normal butyl bromide was prepared by a method given in "Organic Syntheses,"⁸ from *n*-butyl alcohol, hydrobromic acid and sulfuric acid. To obtain the best sample the dried product was distilled in a five-foot column still at atmospheric pressure, the middle fraction being taken from a large run over a range of two-tenths of a degree. The sample used had a density of d_4^0 1.3046 and d_4^{25} 1.2689.

Normal amyl bromide was prepared from synthetic normal amyl alcohol and hydrobromic acid in a manner similar to *n*-butyl bromide, synthetic amyl alcohol being prepared by Grignard synthesis from butylmagnesium bromide and formaldehyde. The dried amyl bromide was fractionated at atmospheric pressure in a manner similar to *n*-butyl bromide, the sample being cut out over a range of two-tenths of a degree. The sample used had the constants d_4^0 1.2431, d_4^{25} 1.2114, n_D^{25} 1.4417.

Normal hexyl bromide was prepared from synthetic *n*-hexyl alcohol and hydrobromic acid-sulfuric acid mixture with a little different procedure than that used for *n*-butyl and *n*-amyl bromides. The synthetic *n*-hexyl alcohol was prepared by Grignard synthesis from butylmagnesium bromide

⁶ Huffman, Parks and Daniels, *J. Am. Chem. Soc.*, **52**, 1549 (1930).

⁷ Nernst, *Ann. Physik*, **36**, 422 (1911).

⁸ "Organic Syntheses," John Wiley and Sons, Inc., New York, 1921, Vol. I, p. 5.

and ethylene oxide. The dried *n*-hexyl bromide was distilled in a five-foot column vacuum still at 90 mm. pressure, the middle fraction being taken out over a range of three-tenths of a degree. The constants of the sample were d_4^{20} 1.1981, d_4^{25} 1.1690, n_D^{25} 1.4452.

The author wishes to express his appreciation to Drs. E. E. Reid, L. M. Ellis, Jr., and P. Borgstrom for their help in the preparation of the compounds.

Results

Radiation effects were thought to give more trouble at 200°K. and above than at lower temperatures. Since any errors due to radiation would show up more in the discontinuous heating method than in the continuous method, it was decided to determine all values below the melting point of the compounds used by the discontinuous method and all above the melting point by the continuous method, as the melting points of *n*-butyl, *n*-amyl and *n*-hexyl bromides occur in the range 160 to 195°K. Table IV gives the heat capacity values for *n*-amyl bromide. Table V gives those for *n*-hexyl bromides.

A transition phenomenon was found to occur with *n*-amyl bromide at about 160°K. (approximately 25° below melting point) in which the calorimeter suddenly heated up about five degrees with no additional energy from

TABLE III
MOLAL HEAT CAPACITY OF *n*-BUTYL BROMIDE
Discontinuous Method

Mean temperature, °K.	Cal./degree	Mean temperature, °K.	Cal./degree
93.14	14.15	186.51	34.54
111.63	15.59	214.03	33.69
125.09	19.45	218.34	31.90
139.07	22.12	240.03	34.10
179.84	34.77	247.29	34.63

Continuous Method (above melting point)

176.93	34.20	227.28	34.48
181.65	33.71	228.81	33.98
187.99	32.86	233.74	33.82
189.96	32.13	235.63	34.06
194.51	34.22	240.22	33.79
196.81	34.50	242.36	34.44
201.15	33.89	246.73	34.12
203.29	33.92	248.96	34.33
207.89	33.73	255.45	34.56
209.62	32.88	259.53	34.92
214.44	32.42	265.97	35.18
215.98	33.78	268.49	35.89
222.36	33.43	279.21	35.44
222.36	33.40	292.31	36.41
		292.31	36.41

TABLE IV
MOLAL HEAT CAPACITY OF *n*-AMYL BROMIDE
Discontinuous Method

Mean temperature, °K.	Cal./degree	Mean temperature, °K.	Cal./degree
95.93	18.86	130.47	24.25
98.92	19.00	148.86	26.26
127.69	24.14	163.36	27.38
Continuous Method (above melting point)			
195.82	39.04	237.06	39.26
203.27	39.82	245.03	39.69
211.64	39.02	251.70	40.32
220.23	39.22	268.48	40.94
228.75	40.24	290.68	41.04

TABLE V
MOLAL HEAT CAPACITY OF *n*-HEXYL BROMIDE
Discontinuous Method

Mean temperature, °K.	Cal./degree	Mean temperature, °K.	Cal./degree
95.32	19.69	147.74	25.29
101.14	20.07	167.51	30.21
123.40	23.60	173.54	32.15
Continuous Method			
213.97	45.52	254.76	46.82
220.70	45.67	261.70	46.76
227.38	45.78	268.62	46.34
234.28	45.23	275.70	47.52
240.93	45.55	282.94	47.84
247.84	45.92	289.80	48.68

the outside and even with the shield temperature five to ten degrees below the temperature of the calorimeter. It was thought from this observation that possibly part of the *n*-amyl bromide formed a glass and this transition was the change from glass to crystal form. Values were then determined from 100–160°K. before the transition was observed and after observing the transition the calorimeter was cooled down again and other values determined on what was thought to be the crystalline form. No appreciable difference was noted in values determined before and after the transition.

No transition was observed in the study of *n*-butyl and *n*-hexyl bromides.

With a large amount of wire in the heating unit benzene (solid) came to equilibrium within two or three minutes after heat was cut off. Solid *n*-butyl bromide with wire strung in the same manner came to equilibrium in three to five minutes and solid *n*-hexyl bromide in approximately the same length of time with the wire spiraled in the heating unit. Solid *n*-amyl bromide took a much longer time to equilibrium with wire wound either way, sometimes as long as ten minutes.

Heats of Fusion

The heats of fusion were determined with the shield and calorimeter at the same temperature while a measured amount of energy was being put into the solid to melt it. The temperature was checked with the difference thermocouple. Each determination was made over a range of approximately six to eight degrees; however, the major portion (about three-fourths) of the total energy required for melting the sample only gave a rise in temperature of a degree near the melting point and the average of this short temperature change was taken as the melting point. Near the melting point the heat capacities of all three substances studied showed considerable increases which were assumed to be due to premelting caused by slight impurities and for this reason all the heat in excess of the normal specific heat values was taken into account in calculating the heat of fusion.

The heats of fusion and the melting points are given in Table VI.

TABLE VI
MELTING POINTS AND HEATS OF FUSION OF *n*-BUTYL, *n*-AMYL AND *n*-HEXYL BROMIDES

	M. p., °K.	Heats of fusion			Average
		1st	2d	3d	
<i>n</i> -Butyl bromide	160.4	2208.7	2230.5	2208.5	2208.6
<i>n</i> -Amyl bromide	185.1	3440.1	3430.6		3435.3
<i>n</i> -Hexyl bromide	188.1	4318.2			4318.2

Entropies

In order to extrapolate the heat capacities curves to 0°K., values were calculated by the use of the Debye equation as adapted by Andrews⁹ to complex molecules. The values for θ_m used were: *n*-butyl bromide, 90.6; *n*-amyl bromide 93.1; *n*-hexyl bromide, 89.7.

Table VII gives the values of the entropies obtained by graphical integration.

TABLE VII
ENTROPIES

<i>n</i> -Butyl Bromide		<i>n</i> -Amyl Bromide	
0-100°K. (solid)	10.24	0-100°K. (solid)	13.58
100-160.4° (solid)	19.96	100-185.1° (solid)	25.26
2208.6/160.4°	13.77	3435.3/185.1°	18.56
160.4-298.1° (liquid)	34.25	185.1-298.1° (liquid)	39.89
	78.22		97.29
<i>n</i> -Hexyl Bromide			
0-100°K. (solid)	13.89		
100-188.1° (solid)	25.79		
4318.2/188.1°	22.96		
188.1-298.1° (liquid)	45.69		
	108.33		

⁹ D. H. Andrews, *Chemical Reviews*, **5**, 533-548 (1928).

Discussion of Results

The molal heat capacities of the solid forms show abnormalities in that the values for *n*-amyl bromide are only slightly lower than those for *n*-hexyl bromide, whereas the values for *n*-butyl bromide are from five to six calories below those for *n*-hexyl bromide. However, the values for the liquid form show a constant difference of approximately six calories between *n*-butyl bromide and *n*-amyl bromide, and *n*-amyl bromide and *n*-hexyl bromide. In each case the curves show nearly constant values up to 40 to 60° above the melting point. This is thought to be due to the breaking down of an association of the molecules. The entropies as calculated show a difference of 19.1 entropy units between *n*-butyl bromide and *n*-amyl bromide and a difference of 11.0 entropy units between *n*-amyl and *n*-hexyl bromide. This variation in difference is due to the abnormally high values for solid *n*-amyl bromide.

The author wishes to express appreciation to Dr. D. H. Andrews for his advice during the course of the research.

Summary

1. An apparatus for the determination of heat capacities by two methods has been built and calibrated and a further comparison of the continuous and discontinuous methods has been made.
2. The heat capacities, heats of fusion, and melting points of *n*-butyl bromide, *n*-amyl bromide and *n*-hexyl bromide have been determined.
3. The entropies have also been calculated.

BIOGRAPHY

Robert Freeman Deese, Jr., the author of this dissertation, was born at Dublin, Ga., October 7, 1902. He received his elementary education in the public schools there. He entered Emory University, Emory, Ga., in September, 1920, and was graduated from this institution in June, 1924, with the degree of Bachelor of Science and the following year received the degree of Master of Science from the same institution. The next two years he taught chemistry at Lambuth College, Jackson, Tenn. He was admitted to the Faculty of Philosophy of the Johns Hopkins University in October, 1927, and has been engaged in research in chemistry toward the degree of Doctor of Philosophy since that time.

